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ABSTRACT

Device-grade TlBr was subjected to various chemical treatments used in room temperature radiation detector fabrication to determine the resulting surface composition and electronic structure. As-polished TlBr was treated separately with HCl, $SOCl_2$, Br:MeOH and HF solutions. High-resolution photoemission measurements on the valence band electronic structure and Tl 4f, Br 3d, Cl 2p and S 2p core lines were used to evaluate surface chemistry and shallow heterojunction formation. Surface chemistry and valence band electronic structure were correlated with the goal of optimizing the long-term stability and radiation response.

INTRODUCTION

The development of room temperature radiation detectors requires new materials with large band gaps and high atomic number species. Thallium bromide (TlBr) meets these requirements having a wide band gap (2.68 eV), high Z (^{81}Tl) along with high resistivity (10^{10} - 10^{12} Ω-cm). In addition, TlBr has long carrier lifetimes (100μs, $\mu\tau_e >$ 5×10^{-3} cm^2/V) and a demonstrated energy resolution of 1.2% at 662 keV. [1-4] However, TlBr detectors are susceptible to polarization phenomena that limit long term performance. [5]

Methods to control this polarization must address vacancy migration, surface chemistry and interfacial reactions at the contacts. Native oxides, surface stoichiometry and surface defects due to polishing all affect device performance. [6] However, the long-term room temperature stability of TlBr gamma detectors has been improved using surface chemical modification but requires further investigation. [7,8]

This paper assesses and discusses the consequences and desirability of various chemical treatments of TlBr. The surface chemistry and surface electronic structure were examined using UV and X-ray photoelectron spectroscopy (XPS). Understanding the surface electronic structure as a function of processing and using it to control the interfacial ionic conductivity has been elucidated with this experimental study.

EXPERIMENTAL

Device-grade TlBr samples were polished and separately immersed in 10% HCl and 10% HF solutions for 60 min. duration, 2% Br:MeOH for 60 sec. duration, all followed by a methanol rinse. A TlBr sample immersed in 96% SOCl$_2$ for 60 min.

duration was rinsed in DI water and blown dry with nitrogen. The chemically modified samples were subsequently transferred for analyses in a vacuum desiccator to preserve surface chemistry.

Quantitative compositional analysis of the resultant surface chemistry was performed immediately with XPS using a monochromatic Al Kα source (1486.7 eV). The 200 μm X-ray beam was incident normal to the sample and the detector is 45° from normal. Core-level spectra were collected with pass energy of 23.5 eV, giving an energy resolution of 0.3 eV that when combined with the 0.85 eV full width half maximum (FWHM) Al Kα line width gives a resolvable XPS peak width of 1.2 eV. Deconvolution of non-resolved peaks was accomplished using Multipak 9.2 (PHI) curve fitting routines with Gaussian-Lorentzian line-shapes and a Shirley background. The collected data were referenced to an energy scale with binding energies for Cu $2p_{3/2}$ at 932.72 +/- 0.05 eV and Au $4f_{7/2}$ at 84.01 +/- 0.05 eV. Binding energies were also referenced to the C 1s photoelectron line arising from adventitious carbon at 284.6 eV. [9]

The UV photoemission spectroscopy was performed at the Stanford Synchrotron Radiation Lightsource (SSRL), Menlo Park, CA. Monochromatic synchrotron radiation from the toroidal grating monochromator equipped beamline 8-1 was used to excite the TlBr. Valence band (VB) photoemission spectra were obtained for each chemical treatment to observe the development of the electronic structure at the surface. The photoemitted electrons were analyzed using a spherical sector analyzer and were measured at normal emission with hν between 50 and 130 eV and an energy resolution of $\Delta E \approx 0.30$ eV.

RESULTS AND DISCUSSION

Quantitative compositional analysis reveals that all of the etched surfaces have oxygen present and are Tl-rich as summarized in Table I. The exception is the HF etched surface that is more stoichiometric but highly oxidized. The HCl and $SOCl_2$ etched surfaces appear more Tl-rich than the polished surface unless the S and Cl are viewed as anions substituting for the Br in the near surface region. For the HCl etched surface, the Tl/(Br + Cl) ratio is 1.15. Similarly for the $SOCl_2$ etched surface, the Tl/(Br + Cl + S) ratio is 1.03. These results suggest that indeed the anion species are substituting for the Br forming a different compound at the surface and thus possibly forming a shallow heterojunction.

Figure 1 presents the Tl $4f_{7/2,5/2}$ core-level spectra for the chemically modified series. From the literature, the Tl $4f_{7/2}$ binding energies for Tl metal, Tl_2O (Tl^{+1}), Tl_2O_3 (Tl^{+3}) and TlBr (Tl^{+1}) are 117.1, 119.1, 118.6 eV and 119.2 eV respectively. [10-14] In addition, the spin-orbit splitting for the Tl 4f peaks is 4.4 eV. Comparing these literature values with the Tl $4f_{7/2,5/2}$ binding energies summarized in Table II, we conclude that the surfaces have oxidized and that the $SOCl_2$, HCl and Br:MeOH treatments initially reduce the Tl surface oxide resulting in the small lower binding energy feature indicative of Tl metal. In addition, the chemical shift indicates supplementary bonding at the surface due to anion substitution resulting in a ternary compound and consequent heterojunction formation.

The Br $3d_{5/2,3/2}$ core-level spectra for the chemically modified TlBr series are presented in Figure 2. The spin-orbit pair peak separation is 1.0 eV (Table II) and the

binding energies are indicative of Br anion in TlBr. [9, 15] Since there is no observed

chemical shift in the Br 3d peak, we conclude that these chemical treatments do not alter

the chemical bonding of the Br, but supports anion substitution and the formation of a

ternary or quaternary compound at the surface, e.g. $TlBr_{1-x}(Cl_{1-y}S_y)_x$.

Select wide scan UV photoemission spectra are presented in Figure 3 for as-

polished TlBr versus photon energy. The binding energies of the Tl $5d_{5/2,3/2}$ spin-orbit

pair summarized in Table III using hν = 60 eV provide a reference for subsequent

changes in surface electronic structure due to chemical treatments. [16-19] Furthermore,

different incident photon energies were used for each etched TlBr surface to distinguish

valence band states (Tl 6s, Br 4p, Cl 3p, S 3p) based on variations in photoionization

cross-sections. [20-24] Specifically, the Br 4p features are visibly resolved in the

spectrum acquired at hν = 60 eV.

Valence band spectra for each chemically treated TlBr surface acquired with hν =

60 eV are presented in Figure 4. The upper valence band (VB) of the as polished TlBr

standard shows features indicative of the Br $4p_{3/2,1/2}$ spin-orbit splitting with some Tl 6s

admixture evidenced by the non-standard Br $4p_{3/2,1/2}$ branching ratio. The small shoulder

on the leading VB edge at ~3.5 eV is assigned to Tl 6p states.

The upper valence band features are modified with each chemical treatment.

Specifically, additional Cl 3p states admix with the Tl 6s states and the S 3p states admix

with the Tl 6p states [21] near the VB edge for the $SOCl_2$ treated surface. At hν = 60 eV,

the Cl 3p photoionization cross-section is larger than that for both Br 4p and S 3p. [19]

However, since the Br concentration at the surface is twice that of Cl, the predominant

features in the valence band are due to the Br $4p_{3/2,1/2}$ spin-orbit pair. [15] Note that the

modified surface electronic structure results in a 1 eV shift of the valence band maxima (VBM) for $SOCl_2$ treated TlBr as summarized in Table III.

Examining the upper valence band of the HCl treated surface, the Br $4p_{3/2,1/2}$ spin-orbit peaks are dominant but have an unusual branching ratio possible due to anion substitution with Cl 3p states. The admixed Tl 6s state provides the broad background for both Br 4p and Cl 3p peaks. In addition, the sharp leading edge of the valence band is attributed to Tl 6p states. Note that the VBM for this chemically modified surface is 0.1 eV lower relative to the as polished surface.

The branching ratio of the Br $4p_{3/2,1/2}$ spin-orbit peaks shown in Figure 4 for the Br:MeOH treated surface is more typical since the compositional analysis revealed this surface to have a Tl/Br of 1.29 (Table I). The VBM for this Br:MeOH modified surface is similar to the as polished surface with a comparable slope to the leading edge.

There are no F states with binding energies in the upper valence band for the HF treated TlBr. In addition, compositional analysis also showed minimal F present. Therefore, the structure at the VBM is attributed to strong Tl 6p emission from Tl^0 followed by emission from Tl^{+1} 6p states. The Br $4p_{3/2,1/2}$ spin-orbit peaks are admixed with Tl 6s states resulting in the observed branching ratio.

Table III also summarizes the width of the photoemission spectra acquired by measuring the secondary electron cutoff and the VBM with the sample biased. Subtracting the width of the entire photoemission spectrum for each treated TlBr surface from the exciting photon energy (hν = 60 eV), the ionization energy E_{ion} has been calculated. Unfortunately we were unable to calibrate the analyzer with clean Au foil during this experiment and thus unable to accurately determine the work function for

each chemically modified surface. However, for reference, the work function ϕ_s for Tl metal is 3.84 eV [25], which is comparable to the calculated E_{ion} as summarized in Table III.

CONCLUSIONS

UV and X-ray photoelectron spectroscopy have been used to examine the surface chemistry and surface electronic structure of chemically modified TlBr. Results indicate that anion substitution at the surface forms a ternary compound that subsequently results in the formation a shallow heterojunction, especially for the HCl treatment. Improved device performance has been noted by increasing the concentration of the HCl, which may indicate further conversion of the surface chemistry with consequent heterojunction formation.

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Table I. Quantitative compositional analysis (atomic %) of chemically modified TlBr

surfaces.

TlBr treatment	Tl	Br	O	Cl	S	F	Tl/Br
As-polished	36.84	33.59	29.57	-	-	-	1.10
$SOCl_2$	34.44	21.75	31.98	9.38	2.44	-	1.58
10% HCl	37.12	22.69	30.54	9.65	-	-	1.64
Br:MeOH	35.85	27.80	36.35	-	-	-	1.29
10% HF	12.60	13.60	73.72	-	-	0.08	0.93

Table II. Tl 4f, Br 3d, S 2p and Cl 2p binding energies (eV) for chemically modified

TlBr surfaces.

TlBr treatment	Tl 4f$_{7/2,5/2}$	Br 3d$_{5/2,3/2}$	S 2p$_{3/2,1/2}$	Cl 2p$_{3/2,1/2}$
As-polished	118.3, 122.7	67.5, 68.5	-	-
SOCl$_2$	118.7, 123.1 117.1, 121.5	67.9, 68.9	166.1, 167.3	197.4, 199.0
10% HCl	118.6, 123.0 116.9, 121.4	67.8, 68.8	-	197.3, 198.9
Br:MeOH	118.7, 123.2 117.2, 121.6	67.9, 68.9	-	-
10% HF	118.2, 122.6	67.6, 68.6	-	-

Table III. Valence band maximum, Tl $5d_{5/2,3/2}$ binding energies and ionization energy

(eV) for chemically modified TlBr surfaces with $h\nu = 60$ eV.

TlBr treatment	VBM	Tl $5d_{5/2}$	$\Delta E_{Tl5d5/2-VBM}$	PE spectrum width	E_{ion}
As-polished	0.40	12.40	12.00	56.2	3.8
SOCl$_2$	1.45	13.30	11.85	56.9	3.1
10% HCl	0.30	12.25	11.95	56.4	3.6
Br:MeOH	0.47	13.00	12.53	57.0	3.0
10% HF	0.45	12.35	11.90	56.2	3.8

Figure Captions

Figure 1.   Tl $4f_{7/2,5/2}$ core-level spectra for the chemically modified TlBr

Figure 2.   Br $3d_{5/2,3/2}$ core-level spectra for the chemically modified TlBr

Figure 3.   Select wide scan spectra for as-polished TlBr versus photon energy

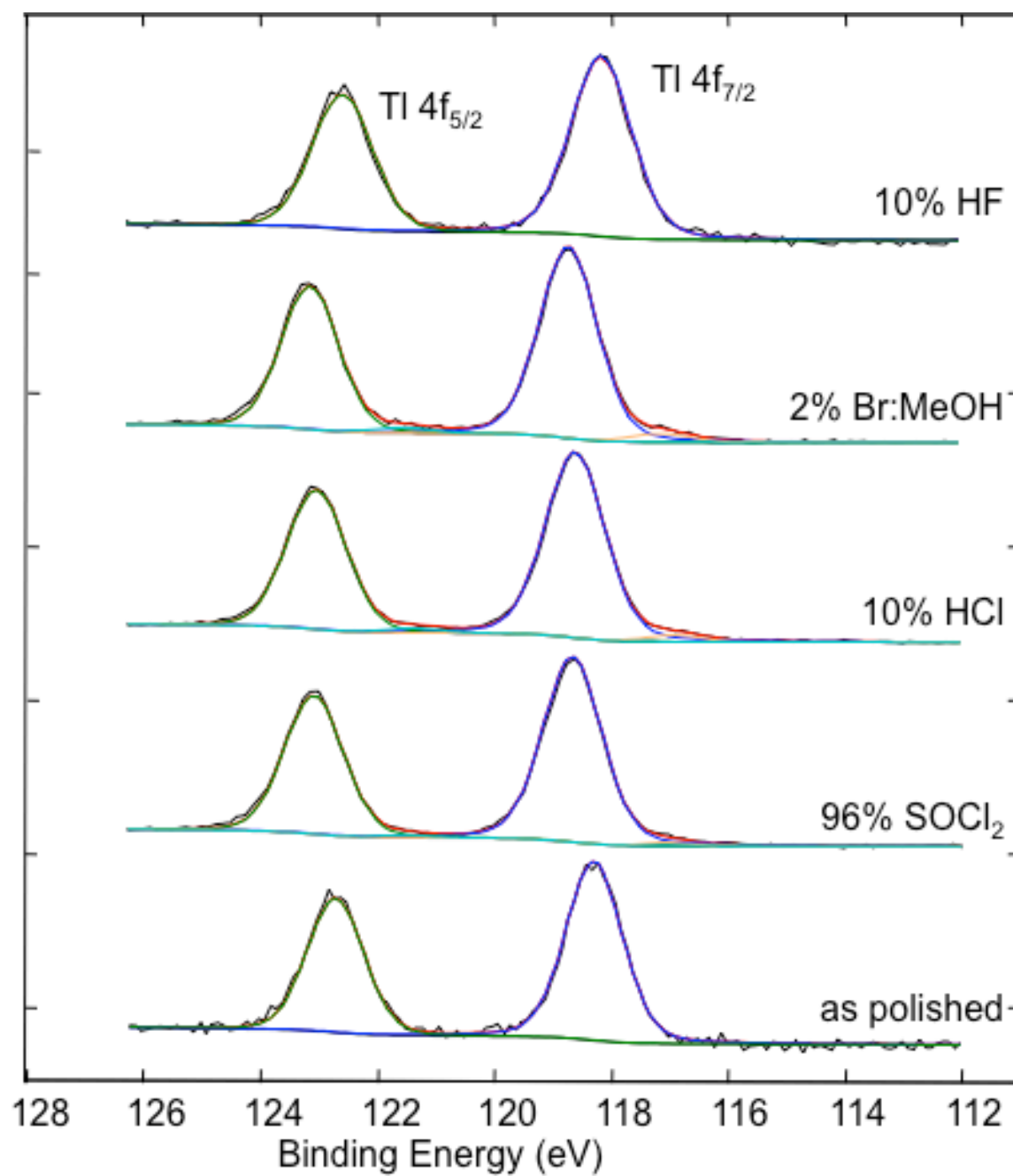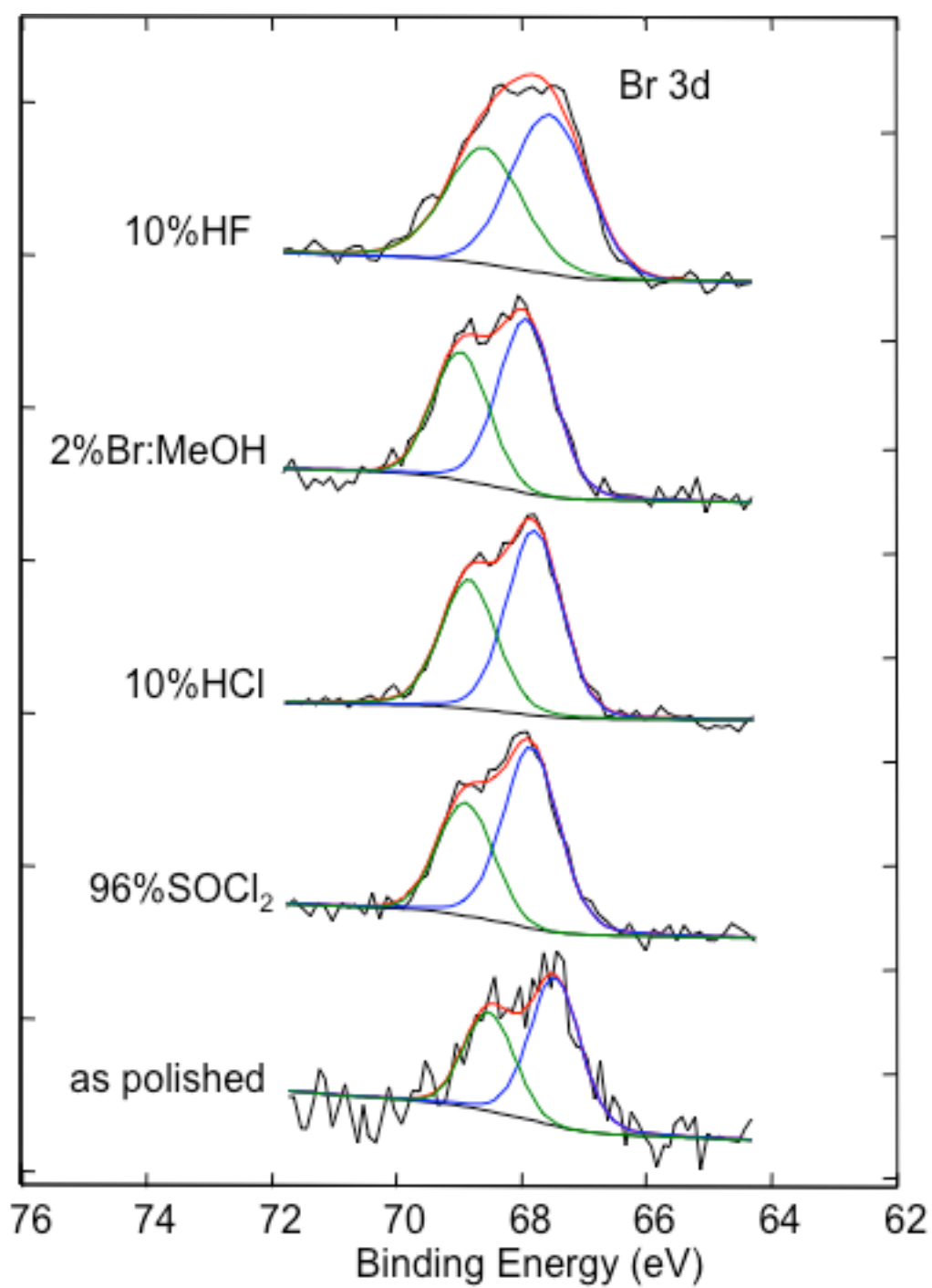Figure 4.   Valence band spectra for each chemically treated TlBr surface acquired
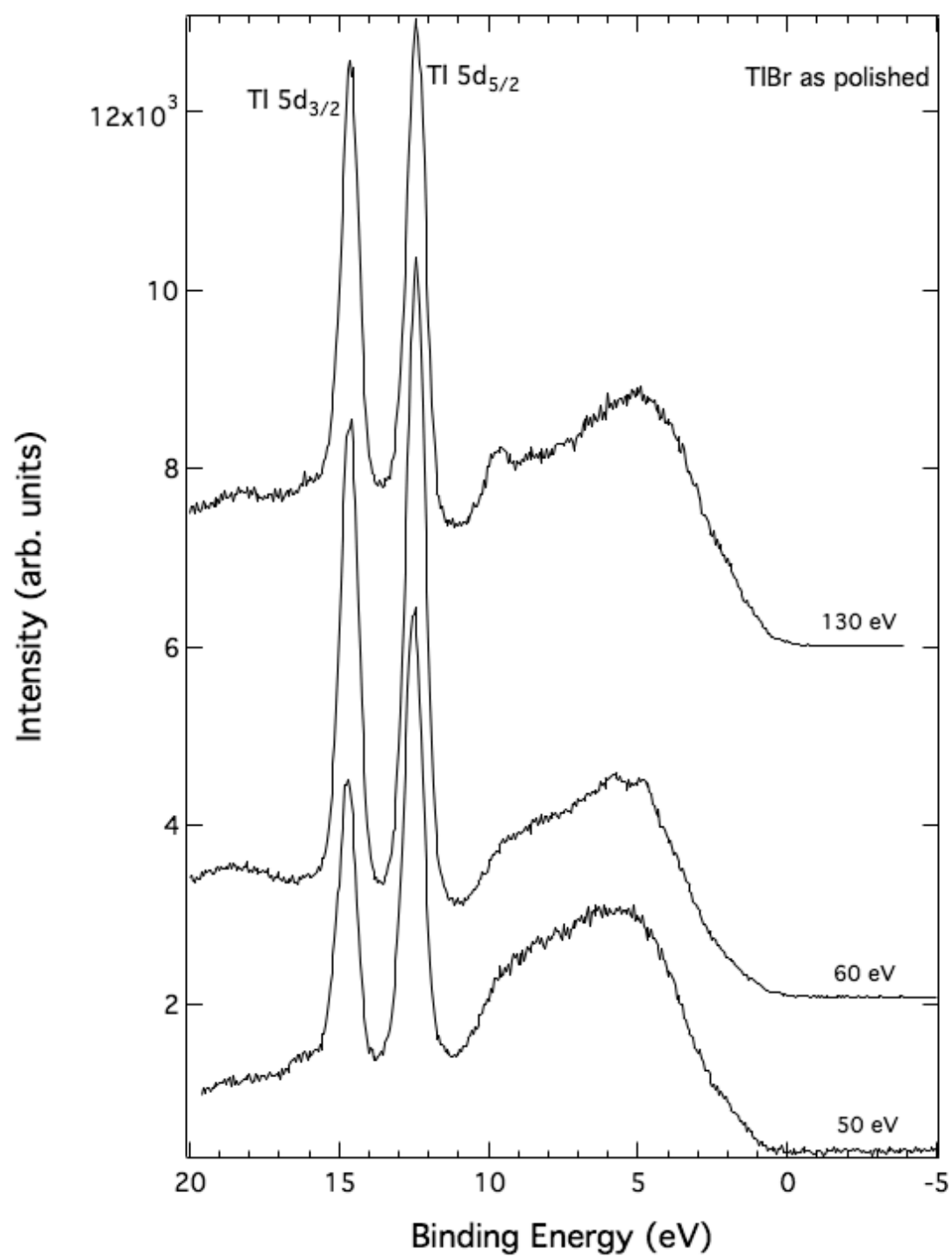
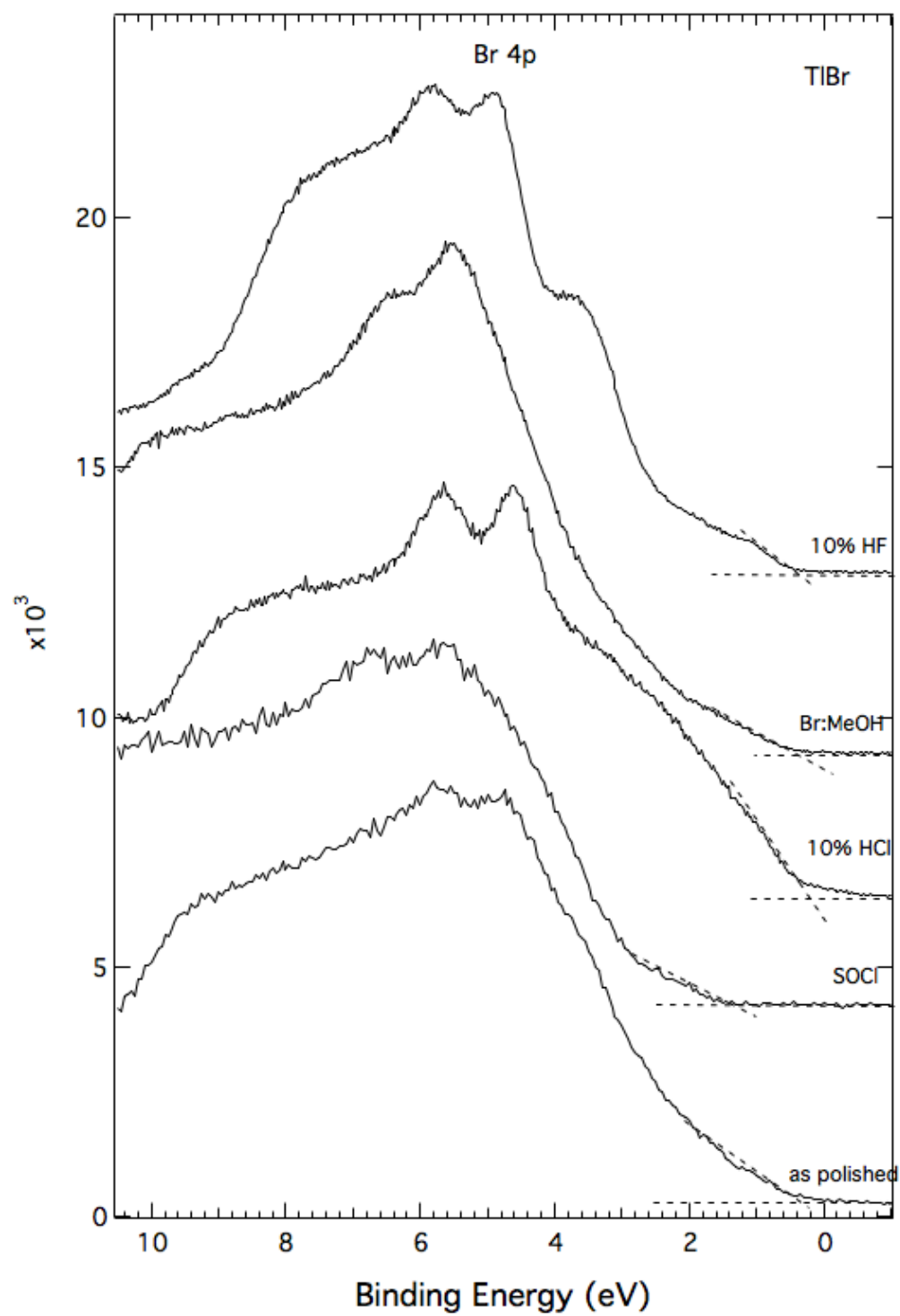with $h\nu = 60$ eV

Figure 1.

Figure 2.

Figure 3.

Figure 4.